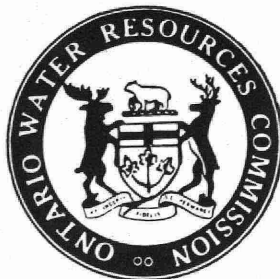


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EVALUATION OF POLYCOMPLEX A-11

AS AN OIL DISPERSANT



DIVISION OF RESEARCH

ONTARIO WATER RESOURCES COMMISSION

June, 1968

R.P. 2020

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**EVALUATION OF POLYCOMPLEX A-11**

**AS AN OIL DISPERSANT**

By:

A. Oda, P. Eng.

June, 1968

Division of Research  
Paper No. 2020

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### SUMMARY

Polycomplex A-11, a non-ionic surface-active organic compound developed recently as an oil dispersant for use in combatting oil pollution was evaluated under laboratory conditions with tests on seven samples of crudes and four grades of fuel oils. It was found to have varying degrees of effectiveness in emulsifying and dispersing various oils under the test conditions. Although found to be biodegradable, it exerted inhibitory effects on the activated sludge at concentrations over one percent. When used as an oil dispersant, it seemed to enhance the biological treatability of crude oils in the sewage treatment process.

Polycomplex A-11 was found to be lethal to fresh water fishes at dosages below 10 ppm and increased the toxicity levels of treated crude oil nearly tenfold.

Odour tests indicated that odours could be detected in tap water containing concentrations as low as 2 ppm Polycomplex A-11. After treatment with this chemical, odours emitted by crude oils were greatly intensified and they became detectable at much lower concentrations.

With some oils, Polycomplex A-11 seemed to work more effectively in salt water than in fresh water.

## INTRODUCTION

With large quantities of crude oil and refined petroleum products being moved daily in networks of pipelines and huge oil tankers involving nearly all kinds of carriers on land and water, there is always a constant threat of an accidental oil spillage. The amount of oil released from any one of these accidents may involve thousands of gallons and even run into millions. This could lead to very serious water pollution problems. This was dramatically illustrated when the ill-fated super oil tanker "Torrey Canyon" was wrecked off the English coast at Land's End on March 18, 1967.

(1) (2) Millions of gallons of crude oil were spilled and spread over hundreds of square miles of the sea, threatening the beaches located along the coastlines of England and Brittany, and destroying nearly all of the marine life in the disaster area.

In the aftermath of the Torrey Canyon incident, several chemicals and materials have been developed and proposed as possible methods to deal with oil pollution of this magnitude. (3) (4) (5) Some of these can be classified as adsorbent materials consisting of booms of rope and straw, powdered tree bark, shredded polyurethane foam, synthetic

textile fibres or any other substance which will adsorb or soak up the oil. In practice, these materials are spread over the oil slicks floating on the surface of the water, gathered together, and then towed ashore for disposal. Others consist of oil dispersants or chemicals which are capable of forming water-soluble complexes with the oil.

Polycomplex A is a well-publicized oil dispersant developed recently by Guardian Corporation. It is said to be capable of solubilizing and dispersing heavy crude and fuel oils in sea water without causing any detrimental effects on the marine life. In addition, it is said to have demonstrated its ability in controlling oil and wastewaters derived from drilling rigs on land and off shore. (5) (6) (7)

While Polycomplex A appears to offer a good preventive method in an emergency to control oil pollution and to remove oil slicks resulting from accidental oil spills, there are some doubts about its performance and possible side effects that may arise from large scale applications in fresh waters, in particular, its influence on water quality and the toxic effects on fresh water fishes.

With this in mind, a sample of Polycomplex A was examined and subjected to various laboratory tests for evaluation.

DESCRIPTION OF POLYCOMPLEX A-11 (PCA-11)\*

Polycomplex A is an organic compound believed to be a non-ionic surfactant developed by Guardian Chemical Corporation but marketed in Canada by Shield Chemical Limited, Toronto. When applied to petroleum oils, either heavy or light, floating on the surface of the water, it forms an oil-complex which breaks down and disperses as micro-sized particles throughout the water under the influence of motion in the form of either as a natural wave action or mechanical agitation.

The original product is said to be highly viscous and very difficult to handle. Therefore, it is diluted to 50% concentration and sold as Polycomplex A-11. Chemical and physical properties of this substance are given in Table I.

\* Most of this information was obtained from supplier's advertising literature (6) (7)

Table I

Physical and Chemical Properties

Active Ingredient	- 47 - 49%
Boiling Point	- about 350°F
Flash Point	- approx. 370°F
(non-flammable except at high temperatures)	
pH of 1% solution	- 9.5 - 9.8
Solubility	- completely soluble in water (including sea water
Specific gravity	- 1.005
Viscosity at room temperature	- 150 - 160 c.p.
Biodegradable, low sudsing, very stable except in strong acids, non-corrosive to steels, non- irritating to eyes or skin (based on 5% solution). Compatible with all types of oil (heavy or light).	



PURPOSE AND SCOPE OF STUDY

The purpose of this study was to conduct laboratory experiments with PCA-11 and various samples of crude and fuel oils in order to obtain some pertinent data that may serve to establish guidelines for its application in the control of oil pollution in fresh waters. These tests were carried out on samples of crudes and fuel oils considered to be representative of those involved in the oil refining processes in Ontario. They were designed to evaluate PCA-11 from the standpoint of:

- (a) its effectiveness as an oil dispersant when subjected to natural wave action and mechanical agitation,
- (b) its biodegradability and biological treatability,
- (c) its toxicity on fresh water fishes,
- (d) its effects on the palatability of water,
- (e) its dispersing action in salt water and fresh water.

## TEST PROCEDURES

### General

All of the tests for the evaluation of PCA-11 were carried out under laboratory conditions utilizing, wherever possible, application techniques outlined in the manufacturer's information brochure (6) (7) and established standard methods (8).

Samples of crude oils and fuel oils given in Table 2 were made available and obtained through the courtesy of the major oil companies and the Department of Energy and Resources Management.

For test purposes, crude oils were selected to include those from Alberta, Saskatchewan and three producing fields in southwestern Ontario. The test samples of fuel oils represented heavy, medium and light grades.

### Effectiveness as an Oil Dispersant

An attempt was made to test PCA-11 on actual oil spills floating on the surface of water being agitated by natural wave action. In order to simulate these conditions, water placed in a shallow rectangular pan was set into motion by means of a Dubnoff Metabolic Shaker. The latter could be easily regulated to move slowly or rapidly in order to provide gentle or vigorous movements of water, similar in effect to the natural wave actions produced on lakes or other bodies of open water.

Table 2

LIST OF OIL SAMPLES TESTED

Sample	Source
<u>Crudes</u>	
Alberta Mixed	Texaco (Canada) Limited
Cambrian*	Clearville, Ontario
Devonian*	Rodney, Ontario
Leduc 852	British American Oil Co. Ltd.
Saskatchewan	Texaco (Canada) Ltd.
Silurian*	Mosa Township, Ontario.
Western (composite)	Shell Canada Ltd.
<u>Refinery Products</u>	
Diesel Oil	Texaco (Canada) Ltd.
Bunker C	British American Oil Co. Ltd.
Furnace Oil	Imperial Oil Co. Ltd.
Kerosene	unknown

\* Ontario crudes supplied by Imperial Oil Co. Ltd. (Chatham office) and Ontario Department of Energy and Resources Management.

With a predetermined volume of oil sample poured onto the surface of the water in the pan, a diluted solution of PCA-11 was sprayed gently on the floating oil slick using a spraying device which was activated by means of a pressurized propellant. This technique helped to break up the solution into a fine gentle spray and is similar in effect to the methods of application suggested by the manufacturer (6).

#### Mechanical Agitation

In another series of experiments, a study was made of the behaviour of various oil samples in water when treated with PCA-11. This was done by applying a concentrated solution of PCA-11 in drops on the surface of an oil slick floating on water and then observing the resultant effects when subjected to agitation with a multiple stirrer.

A sample of oil consisting of approximately 0.5 to 1.0% by volume was placed in a beaker of water and undiluted PCA-11 was applied carefully to the surface, one drop (0.1 ml) at a time. The entire contents were agitated with the stirrer for a few minutes and then stopped. After about five minutes, another drop of PCA-11 was applied and this process was repeated over and over again until all of the oil had been dispersed completely or when sufficient PCA-11 had been added to give a ratio of one part of PCA-11 to five parts of oil.

### Biodegradability Studies

The biodegradable properties of PCA-11 and samples of oil treated with PCA-11 were studied in a small model sewage treatment plant utilizing activated sludge process for the purification of domestic sewage. The plant designed and built by the Division of Research, Ontario Water Resources Commission (9) consisted of a small laboratory model having a capacity of about 50 litres and a retention time of 4 to 6 hours. It is used to determine the treatability of industrial wastes and their effects on the activated sludge process.

For testing purposes, the sewage plant was fed with domestic sewage containing various feed compositions up to 1,000 ppm crude oil and PCA-11-treated oil samples. Its performance was checked by chemical analyses of effluent samples.

In addition to these tests, the biological treatability of PCA-11 and oil samples treated with PCA-11 were evaluated by similar techniques described by Lamb and his associates (10). This involved the use of a respirometer and a membrane-covered oxygen electrode to measure the oxygen utilization rates of an endogenous sludge which had been fed with various samples.

### Toxicity Evaluation

PCA-11, samples of crude oil, and oil treated with PCA-11 were subjected to toxicity evaluation tests by the routine bioassay method prescribed in the STANDARD METHODS utilizing fathead minnows, Pimephales promelas as test animals.

In order to obtain a homogeneous solution, an ultrasonic device was used to fluidize the crude oil in the preparation of a working solution containing 500 ppm crude oil. Similar procedures were followed in making up solutions containing oil treated with PCA-11 except that the crude oil was mixed thoroughly with PCA-11 in the recommended dosage before dissolving in water.

### Taste and Odour Tests

These tests were carried out on a series of tap water samples contaminated with trace quantities of PCA-11, treated and untreated oils to determine their effect on the palatability at very low levels. Standard threshold odours at 60°C were performed on a series of tap water contaminated with odorous substances in the range of 0.2 to 2.5 ppm. Before the odour tests, samples of treated and untreated oils were homogenized with the ultrasonic equipment.

Taste tests were performed on samples containing PCA-11 only and thus the results are therefore intended to be qualitative.

### Effect of Salt on the Dispersing Action

The information provided in the manufacturer's brochure seems to imply that PCA-11 works more effectively in brackish waters. For this reason, it was decided to investigate the effect of salts in the water on the dispersing action of this chemical. This was done by conducting parallel agitation tests concurrently on saline and fresh waters and then comparing the results obtained.

The test samples were prepared in the range of salt concentrations likely to be found in sea water.\* These were as follows:

Sample No. 1	- 0%	NaCl in tap water
2	- 1%	
3	- 3.5	
4	- 5.0	

A test sample of oil, approximately 1% by volume, was placed in each of the above solutions. PCA-11 solution was applied and oil water mixtures were agitated simultaneously as described above in "Mechanical Agitation".

Samples of oils including Alberta Mixed, Cambrian, Leduc 852, and Saskatchewan crudes along with Bunker C fuel oil were studied in these tests.

\*Highest salinity in the oceans has been recorded in the Red Sea reportedly to be in the range of 3.7 to 4.1% and the lowest in the Baltic Sea from 0.2 to 0.7%. In the Atlantic Ocean, it rises to about 3.75% in the northern subtropical region with average values of 3.50 to 3.55% prevailing in the northern parts. (11)

## GENERAL OBSERVATIONS AND SUMMARY OF TEST DATA

### Laboratory Examination and Analyses

The results of laboratory analysis utilizing infra-red spectroscopic techniques have indicated that the main active ingredient in PCA-11 was found to be a condensation product of ethylene oxide and a straight-chain alcohol. This product is a non-ionic surface active agent which is capable of solubilizing petroleum oils and their derivatives in water. It is also one of the main constituents in the formulation of many detergents widely used industrially for cleaning oil tanks and other similar applications as well as for suppressing foams and breaking emulsions (12).

When mixed together in undiluted form with various crude oils, PCA-11 had a tendency to form precipitates consisting of a soft paraffin-like material. With the addition of water, the precipitate appeared to break up readily and improve the compatibility of oil with water.

### Effectiveness as an Oil Dispersant

All of the oil samples were found to react immediately with PCA-11. When sprayed, the floating oil slicks appeared to break up into small globules of oil which seemed to move away quickly from the application area and collect near the



water-line on the walls of the pan. With agitation, either in a Dubnoff shaker or simply by stirring the water, the small oil slicks began to disintegrate into smaller particles which dispersed very readily in the water. The dispersion of these particles in the water was observed to continue as long as there was some agitation. However, when the agitation was discontinued and the oil/water mixture allowed to stand for any length of time, the dispersed oil particles had a tendency to rise to the surface and conglomerate into an oil slick again. There was no difficulty involved in redispersing the reconstituted oil slick with a minimum amount of agitation.

#### Tests with Dubnoff Shaker

Most of the oil samples tested were found to react and disperse immediately when sprayed with PCA-11 solution and subjected to gentle agitation by the shaker. The action of emulsion and dispersion was greatly hastened by more vigorous agitation and continued application of PCA-11.

Except for Bunker C, it was found virtually impossible to obtain a complete emulsion with most oil samples tested regardless of the agitation or the amount of oil dispersant applied. In many cases, the oil slick had a tendency to come into contact with the walls of the test pan and cling

tenaciously throughout the duration of the test. Most of the oils disintegrated into small droplets and then moved back and forth on the crest of waves caused by shaking movements.

Bunker C oil is a very thick viscous material which stays together as an amorphous mass and remains afloat when dumped into the water. With the application of oil dispersant and gentle agitation, it became fluidized and dispersed slowly into the water. Once disintegrated, the small particles of oil did not rise to the surface. They remained well-dispersed and formed a homogenized oil/water mixture.

The observations from the tests with the other oils were somewhat similar to those noted in the mechanical agitation tests involving a multiple stirrer. These are recorded and discussed below.

#### Mechanical Agitation Tests

The observations from these tests are recorded and tabulated in Table 3. Most of the oil samples responded very well to treatment with PCA-11 and subsequent agitation. Despite the increased dosages of PCA-11, it was impossible to complete emulsification with most of the oil samples tested in such a way that the oil particles would remain well-dispersed for any length of time. Bunker C oil was found to be the only sample that could be dispersed very readily.

Table 3

SUMMARY OF OBSERVATIONS AND TEST DATA OBTAINED  
FROM MECHANICAL AGITATION TESTS

<u>Sample</u>	<u>PCA-11 Dosage</u>	<u>Observations and Remarks</u>
Alberta Mixed	1:5	not completely emulsified
Cambrian	1:4	not completely emulsified
Devonian	1:4	not completely emulsified
Leduc 852	1:4	good emulsion with oil slick
Saskatchewan	1:5	good emulsion with oil slick
Silurian	1:4	not completely emulsified
Western (Shell)	1:5	not completely emulsified
Bunker C	1:10	completely emulsified
Diesel	1:10	good emulsion
Furnace	1:10	good emulsion
Kerosene	1:10	good emulsion

Notes: PCA-11 Dosage indicates the actual amount applied and is expressed as a ratio of the oil dispersant to the oil.

Good emulsion and oil dispersion became apparent with the rapid discoloration of the oil/water mixtures. The darkest discolorations were noted in samples with Bunker C, Saskatchewan crude and Alberta mixed and Western composite crudes.

PCA-11 was found to be particularly effective with Bunker C oil. The latter began to break up very quickly into globules after the application of a few drops. The globules became progressively smaller and smaller with each successive addition of PCA-11.

Lighter grades of fuel oils such as diesel, furnace and kerosene appeared to break up quickly after the addition of a few drops of PCA-11 but the water became cloudy and tended to obscure the inherent colour of the oil samples.

One interesting observation was made in these tests. It was found with the addition of sufficient dosage of oil dispersant and subsequent agitation, any oil adhering to the walls of the test pan could be removed eventually.

#### Biodegradability Studies

Table 4 gives chemical data derived from a preliminary study involving crude oil and PCA-11 on sewage treatment processes. These data were intended to show the comparative

Table 4

CHEMICAL ANALYSIS OF SAMPLES  
FROM THE MODEL SEWAGE TREATMENT PLANT

Run No.	Particulars	BOD	COD	pH	Solids		
					Total	Diss.	Susp.
1	Raw sewage only	205	575	7.63	940	769	171
	a) effluent	16	57	7.40	-	742	-
	b) effluent	11	57	7.60	-	702	-
2	Sewage + 100 ppm oil	370	521	7.75	931	662	269
	effluent	18	60	7.40	-	686	-
3	Sewage + 100 ppm oil (treated)	280	595	7.91	994	660	334
	effluent	11	55	7.70	-	656	-
4	Sewage + 100 ppm oil (treated)	230	635	7.65	818	635	174
	effluent	33	60	7.50	-	612	-
5	Sewage + 1000 ppm oil	225	790	7.65	1104	900	204
	effluent	86	224	7.50	942	828	114
6	Sewage + 1000 ppm oil (treated)	-	-	-	-	-	-
	effluent	58	98	7.50	778	768	10

Notes:

- (1) The data for raw sewage in Run No. 1 represent average analytical values of samples collected. These were in the following range:  

BOD - 160-230 ppm      Solids - Total      - 818-1104 ppm  
COD - 300-790 ppm      - Dissolved      - 644- 900 ppm  
pH - 7.60-7.65      - Suspended      - 136- 204 ppm
- (2) Effluent analyses were performed on the supernatant decanted from settled samples.
- (3) Alberta mixed crude oil was employed in these tests except in Run No. 4 where Saskatchewan crude was used.
- (4) For "treated oil" samples, the crude oil was mixed with PCA-11 in the ratio of 1 part PCA-11 to 5 parts of crude oil and then added to the raw sewage in approximate dosage as a feed to the model sewage treatment plant.

Table 5

SUMMARY OF BIOLOGICAL TESTS - TOXICITY EVALUATION

(1) Results of Bioassay Tests

<u>Sample</u>	<u>4-hr</u>	<u>TL<sub>m</sub> Concentration, mg/l</u>		
		<u>24-hr</u>	<u>48-hr</u>	<u>96-hr</u>
PCA-11	-	2.5 to 25	-	-
Untreated crude	-	630	520	250
Treated crude	-	65	62	46

- Notes: 1) TL<sub>m</sub> concentration represents medium tolerance limit on the concentration at which 50 percent of test animals may survive. It is obtained by interpolation of experimental data related to the observed number of test animals surviving at the end of the given time of exposure in the test samples.
- 2) TL<sub>m</sub> values given for PCA-11 were determined by means of range tests.
- 3) Alberta mixed crude oil was used as a test sample. It was fluidized into solution of 500 ppm with an ultrasonic probe system.
- 4) Crude oil was treated in the ratio of 1 part of PCA-11 to 10 parts of oil.

(2) Test Conditions

Nature of test - Static Bioassay

Description of Dilution Water - Toronto tap water

Hardness - 140 ppm as CaCO<sub>3</sub>

pH - 8.3 - 8.75

Ambient temperatures - 20.3 to 22.1°C

(3) Description of Test Animals

Species - Pimephales promelas (fathead minnows)

Number Used - 5 per 10 litre of sample

Length - Maximum - 6.2 cm

Minimum - 4.6 cm

Average - 5.0 cm

Weight - Range - 0.4 to 1.30 gm

Average - 0.70 gm per fish

Weight of fish - 0.34 gm per litre

\*Tests performed by Biology Branch, Division of Laboratories, Ontario Water Resources Commission

biodegradability of treated and untreated crude oils present in domestic sewage at concentrations of 100 ppm and 1,000 ppm evaluated from the standpoint of BOD and COD analyses. Only two samples of crude oil were tested. There was no attempt to carry out a complete survey on various samples nor to assess their effects on the biological processes at various concentrations.

The data pertaining to oxygen utilization rates determined by continuous measurements of dissolved oxygen content in an endogenous sludge with samples of PCA-11 and crude oil are presented in Figures 1 and 2.

#### Effect of Salt on the Dispersing Action

The best dispersion was observed in test samples with higher salt concentrations. This was also manifested by the darker discolorations appearing in the salt solutions after treatment.

Except for the Cambrian crude, the oil dispersant began to take effect more rapidly in salt solutions in most oil samples. With the Cambrian crude, the dispersion seemed to occur more readily in fresh water but ultimately, the best results were observed in the 5% salt solution.

Saskatchewan crude began to disperse first in the 5% salt solution with the slowest reaction taking place in the fresh water. It is also interesting to note that in spite of the best dispersion occurring in the 5% salt solution indicated by its dark colour, most of the surface in this sample was covered with an oil slick, while in the fresh water, the amount of oil slick was at a minimum.

Alberta mixed crude and Bunker C oils were two samples which dispersed completely in salt solutions. It was noted that there was practically no oil slick floating on the surfaces of test samples containing 3.5 and 5% salt at the end of the tests.

From these observations, it can be generally concluded that the PCA-11 works more effectively as an oil dispersant in salt water than in fresh water.



## DISCUSSION OF RESULTS

### Effectiveness as an Oil Dispersant

The data presented in Table 3 show the observations and results recorded in the mechanical agitation tests involving the treatment of various oil samples in tap water with PCA-11. These are also applicable to the tests involving Dubnoff Shaker.

Only the fuel oils were found to disperse very readily at the recommended dosage of 1-10. All of the other oils required much higher dosages and in spite of this, did not yield completely to treatment with PCA-11. Leduc 852 and Saskatchewan crude oils showed the best results of emulsification but very small oil slicks began to appear on the surface of oil/water mixture during the quiescent periods.

It is apparent that the effectiveness of PCA-11 as an oil dispersant is largely dependent upon the chemical and physical characteristics of various oil samples. This important observation has been acknowledged in the literature provided by the manufacturer of this chemical (6). Unfortunately, time and the lack of analytical facilities did not permit further study into this aspect of the investigation, namely to determine what chemical and/or physical properties governed the reaction between the crude oil and the oil dispersant.

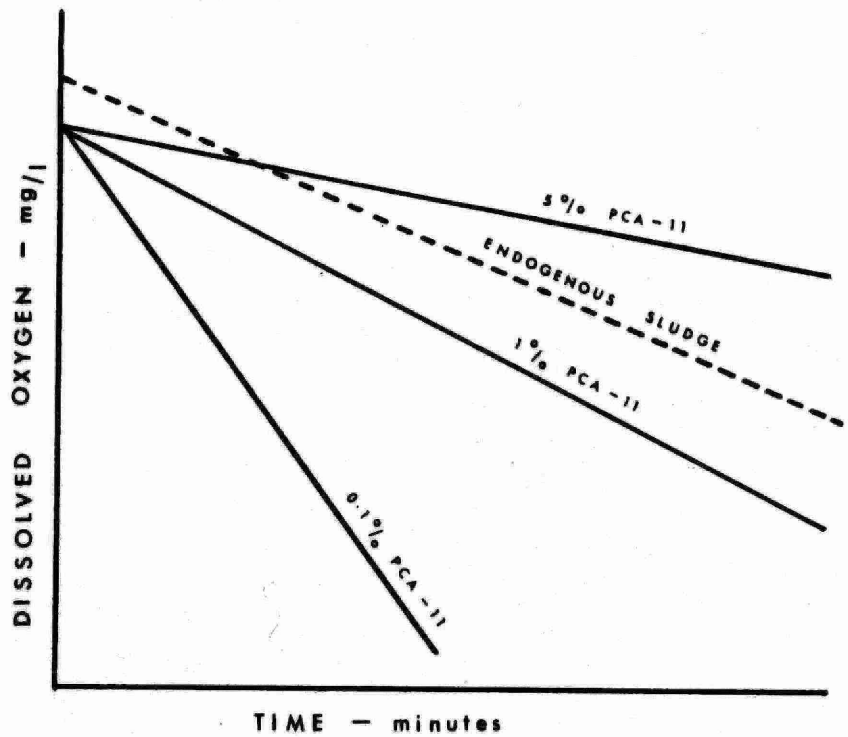
### Biodegradability Studies

Chemical data given in Table 4 show the comparative effects imposed on the effluent quality as a result of feeding domestic sewage mixed with treated and untreated crude oil in a sewage treatment process.

A comparison of data obtained in Runs No. 2 and 3 will indicate a slight improvement in the effluent quality measured in terms of BOD and COD values resulting from the use of PCA-11. It is noted that the effluent quality from Run No. 3 was comparable to that of Run No. 1 which was operated on raw sewage only.<sup>®</sup> The beneficial effects of PCA-11, may be more evident in Runs No. 5 and 6 which were operated with feeds containing 1,000 ppm crude oil. It can be seen that BOD and COD values in the effluent from Run No. 6 are significantly lower. This indicates very clearly that use of PCA-11 as an oil dispersant greatly enhanced the biological treatability of crude oil in the activated sludge process under the test conditions.

Biodegradability of PCA-11 and oil samples, both treated and untreated, was also evaluated by the use of data pertaining to oxygen utilization rates of an endogenous sludge in contact with these substances. These data are illustrated in Figures 1 and 2.

FIGURE 1

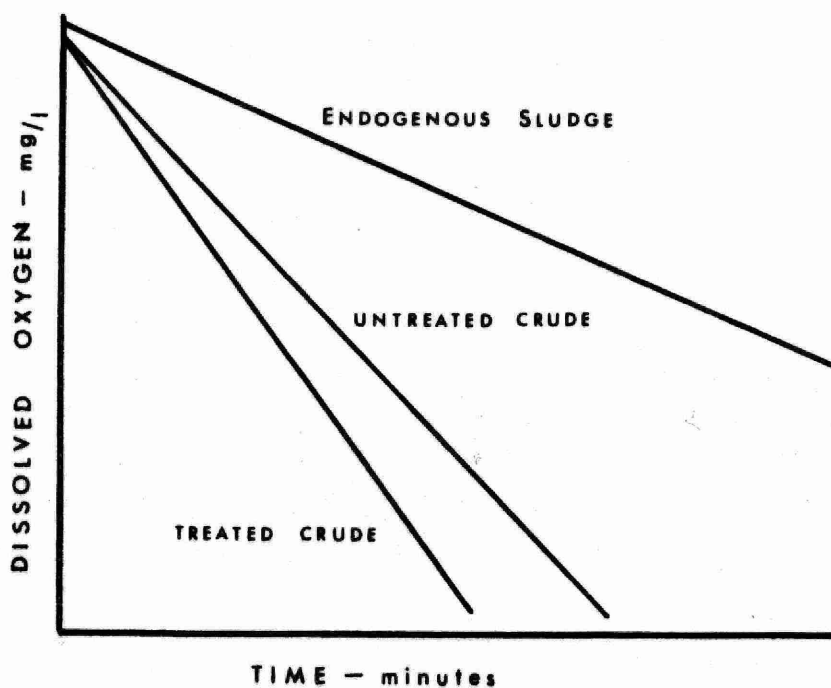


Curves Showing Oxygen Utilization Rates of an Endogenous Sludge with Various Concentrations of PCA-11

Figure 1 shows the curves reflecting the depletion patterns of dissolved oxygen when various concentrations of PCA-11 were added to the endogenous sludge. Curve designated as 0.1% PCA-11 shows a rapid depletion of dissolved oxygen indicating an increased activity of the organisms in metabolizing the oil dispersant in the sludge. At higher concentrations of PCA-11, the respiration rates tended to be somewhat similar in pattern to that of an endogenous sludge and this is illustrated by the 1% PCA-11 curve. This indicates that at a concentration of approximately 1%, PCA-11 had no apparent effect on the activity of the organisms in the sludge. However, at 5% concentration, a much lower rate of activity was exhibited by the organisms as shown by higher levels of dissolved oxygen content in the sludge. This means that at this concentration, the PCA-11 may have been slightly toxic and therefore exerted a slight deleterious effect on the organisms.

Figure 2 shows the curves representing the respiration rates of endogenous sludge after the addition of treated and untreated crude oils. It can be seen that there was a slight improvement in the biological treatability of crude oil which had been treated with PCA-11.

FIGURE 2



Curves Showing Oxygen Utilization Rates of an Endogenous  
Sludge with Treated and Untreated Crude Oil  
at a Concentration of 1,000 ppm

(Crude Oil treated with oil dispersant at a ratio of  
1 part of PCA-11 to 5 parts of oil)

### Toxicity Evaluation

The results of preliminary range tests indicated that PCA-11 alone was found to be significantly toxic to fishes at relatively low concentrations. At concentrations over 250 ppm PCA-11, total mortality occurred within 30 minutes; at 25 ppm PCA-11, all of the fishes died within 6.5 hours while those exposed to a test sample with 2.5 ppm PCA-11 were found to be still alive after 72-hour exposure.

Similar observations were reported by the Michigan Water Resources Commission on the bioassay studies carried out with bluntnose minnow (Pimphales notatus) approximately 5.5 cm in length. The report concluded that the  $TL_m$  value for these species should fall in between 1.0 ppm and 10 ppm with the most probable value of 3.2 ppm (13).

The results of the bioassay tests are tabulated in Table 5. The data indicates  $TL_m$  values for Pimephales promelas were estimated to be 630 ppm untreated crude oil for a 24-hr exposure and 250 ppm after a 96-hr exposure. With the use of PCA-11, toxicity of the treated crude oil was increased very markedly as the  $TL_m$  values dropped very sharply to one tenth of the value for that of the untreated crude.

### Taste and Odour Tests

PCA-11 has a faint perfumic type odour which could be described as being sweet and pleasant and somewhat reminiscent of the subtle fragrance emitted by household liquid detergents. At a concentration of 1,000 ppm in tap water, its odour was quite perceptible. Routine threshold odour tests at 60°C indicated that trace quantities as low as 1.0 ppm were detectable while at concentrations of 1.5 to 2.0 ppm, characteristic odours of this chemical were found to be discernible.

It was found that PCA-11 has a tendency to intensify odours of crude oil when treated. This was demonstrated quite clearly in the odour tests involving samples of water containing very low concentrations of treated and untreated oil solubilized by the ultrasonic equipment. Samples containing 0.2 ppm treated oil gave off more intense odours than those observed in samples with 0.5 ppm. No attempt was made to establish the limit of detectability for minimal concentrations.

At a dilution of 1:4, PCA-11 has a very sharp bitter taste but in a water sample containing 1,000 ppm, the taste was hardly detectable. Its flavour was somewhat reminiscent of household detergents. However, this observation was believed to be influenced by the odours emitted by the sample. No detectable tastes were apparent in samples containing concentrations below 100 ppm.

### CONCLUSIONS

Based on the results of the evaluation tests carried out under laboratory conditions, these are some of the principal findings:

(1) Polycomplex A-11 is a non-ionic surface active agent consisting of a condensation product of ethylene oxide and straight-chain alcohol. The product was found to be mutually soluble with all of the oil samples tested.

(2) When applied under suitable conditions, the chemical exhibited varying degrees of effectiveness in emulsifying and dispersing oils in water.

(3) After treatment with an appropriate chemical dosage, only a minimum amount of agitation was required to keep the oil emulsified and well-dispersed. However, as soon as the agitation was discontinued, the dispersed particles of oil had a tendency to rise slowly and conglomerate into an oil slick on the surface.

(4) Most of the oil samples responded very well to treatment with a recommended dosage of 1-10, but in some cases, it was found impossible to achieve complete emulsification even with the use of much higher dosages.



(5) Bunker C fuel oil and heavy Saskatchewan crude were two samples tested which reacted very well with this chemical. They remained well-emulsified long after treatment.

(6) The chemical was found to be readily biodegradable at reasonably low amounts but in concentrations over one percent, it appeared to exert some inhibitory effects on the biological activity of the microorganisms in activated sludge.

(7) The use of this chemical seemed to enhance the biodegradability of crude oil in an activated sludge process.

(8) The chemical was found to be very lethal to fathead minnows, Pimephales promelas at concentrations between 2.5 ppm and 25 ppm.

(9) The toxicity levels expressed in terms of  $TL_m$  values increased nearly tenfold in the samples of crude oil treated with this chemical.

(10) At very high concentrations, the chemical imparted a very sharp bitter taste to water but was hardly detectable at concentrations below 1,000 ppm.

(11) Threshold odour tests at 60°C indicated that odours could be detected in samples of tap water containing less than 2.0 ppm of this chemical.

(12) Treatment with this chemical had a tendency to enhance and intensify any odours emitted by the crude oil so that they become more detectable at much lower concentrations.

(13) The dispersing action of the chemical on crude oils seemed to be more effective in salt waters than in fresh waters.

### RECOMMENDATIONS

There is no doubt that oil dispersant chemicals such as Polycomplex A-11 have a definite value in minimizing oil pollution problems and removing unsightly oil patches floating on large bodies of open waters. However, the results of this investigation have revealed that this chemical is lethal to fresh water fishes at relatively low concentrations. In addition, it has a tendency to affect the palatability of water supplies if present in trace quantities. Because of these adverse effects, great care should be taken to insure that the quantity of chemical used is kept to a minimum and its application should be made with utmost discretion and be limited to the control and abatement of oil pollution only in emergency situations.

Polycomplex A-11 has been found to be very effective in dealing with some particular types of oils but has shown only limited success with others. Therefore, it should not be assumed that this oil dispersant will be universally applicable to all situations. Other chemical formulations that are available commercially as oil dispersants should be tested thoroughly with various oil samples in order to obtain some background information so that a suitable chemical can be selected in an emergency.

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